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Preparation and Performance of Conductive Copper Ink Based on Chemical Deoxidization

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This paper adopts the improved liquid-phase chemical deoxidization to prepare nano-copper powder used as principal conducting material instead of nano-silver particles in conductive ink of printed electronics. The prepared nano copper particles are analyzed for their microstructure and electrical conductivity. Studies show that the prepared nano-copper particles are mainly distributed chain-like, with an average particle size of 26 nm, of which, those with 20-25nm amount to 42%, 25-30nm to 29%. The PVP surfactant can effectively organize the oxidation of nano-copper. After the sintering temperature exceeds 412°C, the organic materials mixed in the nano-copper have completely volatilized. The content of nano copper decomposition product hits upon 46.5% of the original sample. The higher the sintering temperature, the lower the sheet resistance of the conductive copper film. After the sintering temperature exceeds the melting point of nano-copper, a stable conductivity channel will be formed on the surface of the film. Subsequently, continuous sintering of the film has an insignificant effect on its conductivity.

1. Introduction

In the past century, a plurality of electronic products were made from micron-level electrocondution slurry. With the progressive advancement of modern technology, current electronic products tend to be refined, small-sized, flexible, and highly integrated. Up to now, the traditional micron-level electrocondution slurry has fallen well short of what's needed (Kumashiro et al., 2009; Zhang et al., 2009).

Conductive ink for printed electronic technology is the core material of the current electronic printing industry and has been widely applied in many fields such as RFID, electronic product monitors, batteries, printed circuits, etc. (Sergeev et al., 2018; Dang and Fribourgblanc, 2013). In the past, there are some gaps such as a lot of industrial waste water, high costs, and low efficiency in the manufacture technologies for conductive inks. Nano-metal-based conductive ink emerges to effectively fill the above gaps. Some fine electronics can be efficiently printed out with various types of conductive materials (carbon nanotubes, graphene, conductive polymers, nano-metals (Cui et al., 2010; Kumar et al., 2009; Titkovr et al., 2015; Dang and Fribourgblanc, 2015; Tam et al.,2016; Yang et al., 2013). Due to expensive cost of heavy metals such as carbon nanotubes, graphene, gold and silver, the concept that the nano copper particles are used as a conductive ink has been the future trend of R&D in the field (Lee et al., 2006; Tang et al., 2010; Lim et al., 2015; Yang et al., 2012).

Currently, Nano-copper particles are mainly prepared by gas-phase evaporation, electrolysis, plasma coagulation, mechanical grinding and other methods (Lee et al., 2009; Joo et al., 2014). However, the copper ions available by the above methods are easily oxidized and unstable (Zhang et al., 2014). This paper adopts an improved liquid-phase chemical deoxidization to prepare nano-copper powders used the principal conducting materials to replace nano-silver particles in conductive inks (Haneda and Towata, 2015). The prepared nano copper particles are analyzed and explored for their microstructure and conductivity. Here, the conclusions can provide a new idea for the development of printed electronics.

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2. Preparation of nano-copper-based conductive ink

Raw materials: copper chloride dihydrate, hydrazine hydrate, ammonia hydroxide, sodium hydroxide, polyvinylpyrrolidone, trimethylammonium bromide, ascorbic acid, carboxylated carbon nanotubes.
Test instrument: ultrasonic cleaner, magnetic electric mixer, electronic scale, centrifuge, vacuum drying oven, electron microscope, X-ray diffractometer.
The process for preparing nano-copper powder based on the liquid-phase chemical deoxidization is shown in Fig. 1.
Chemical reaction process of nano copper conducting ink:
The hydrazine hydrate in the solution acts as an oxidant and a reductant for chemical reaction, respectively. The reaction process is given as follows:

$$2NH_2+2OH^-=N_2H_4+2H_2O+2e \quad (1)$$

$$N_2H_4+4OH^-=N_2+4H_2O+4e \quad (2)$$

In practices, the nano-copper colloids are prepared mainly by Eq. 2, pH>9, and the reduction reaction of Cu2+ can be expressed as

$$2Cu^{2+}+4e=2Cu \quad (3)$$

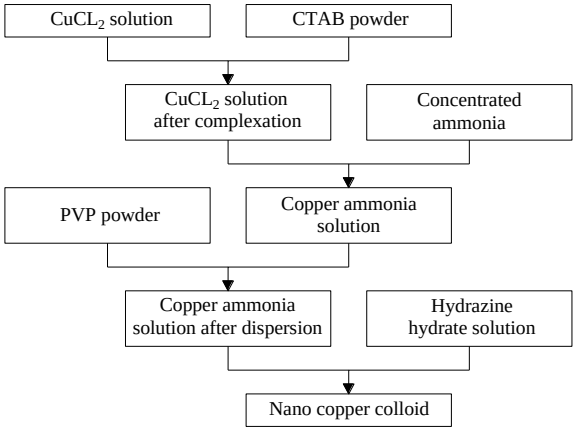

Figure 1: Preparation process of nano-copper colloids

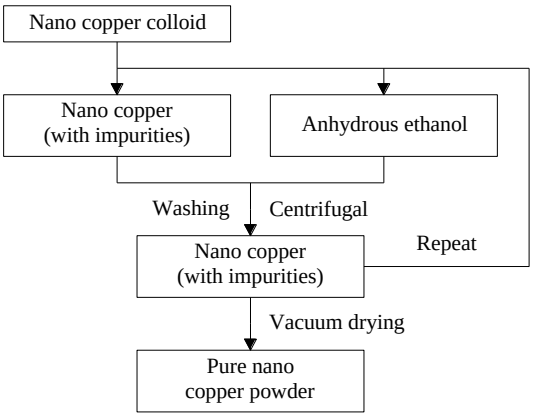

Figure 2: Preparation process of nano-copper powder

According to the relevancy theory of thermodynamics, the free energy $\Delta G<0$ in the reaction process, then the following equation is true:

$$E_1=0.56-0.05412pH \quad (4)$$

$$E_2=0.36-0.02708\lg\left[Cu^{2+}\right]=0.1458V \quad (5)$$

$$\Delta G=E_2-E_1=0.05412pH-0.4142 \quad (6)$$

According to Eqs. 1~6, the nano copper in the reaction solution is prepared by the following formula:

$$2Cu\left(NH_3\right)_4^{2+}+N_2H_4\cdot H_2O=2Cu+N_2+4NH_3+4NH_4^{+}+H_2O \quad (7)$$

The resulting copper colloids prepared by Fig. 1 are subjected to secondary treatment in the process as shown in Fig. 2. Nano copper powder is obtained after the treatment.

3. Detection and analysis of nano-copper properties

As shown in Fig. 3, the X-ray diffraction pattern is plotted for the prepared nano copper powder. It is obvious that the diffraction peaks of the copper crystal appear at 2θ=42.9°, 2θ=50.8° and 2θ=73.8°, respectively; while the diffraction peaks of the copper oxide crystal appear at 2θ=36.2°. It is testified that film on the nano copper powder surface exists as Cu2O. The nanoparticles mainly distribute chain-ball-like.

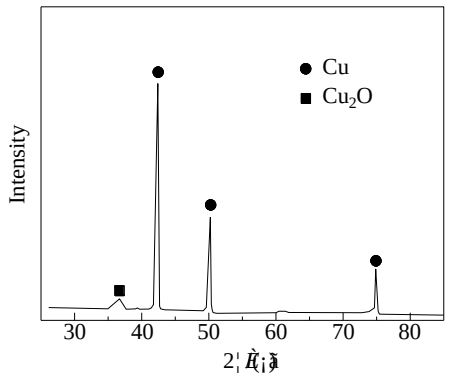

Figure 3: X-ray diffraction pattern of nano copper powder

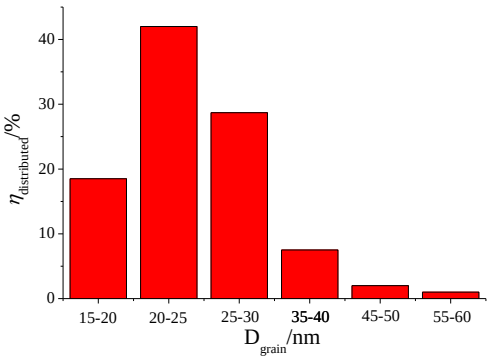

Figure 4: Statistics of nano copper particle size distribution

As shown in Fig. 4, the sizes of the prepared nano copper particles are counted up. on the whole, the average particle size of nano copper is 26 nm, those with 20-25 nm reaches up to 42%, and the 25-30 nm is 29%.

As shown in Fig. 5, the results from the analysis of nanoparticles are obtained using an infrared spectrum analyzer, see Fig. 5 (a) for the infrared spectrum of the nano copper particles after secondary treatment; Fig. 5 (b) for the infrared spectrum of the original nano copper particles, and Fig. 5 (c) for the infrared spectrum of the PVP dispersant.

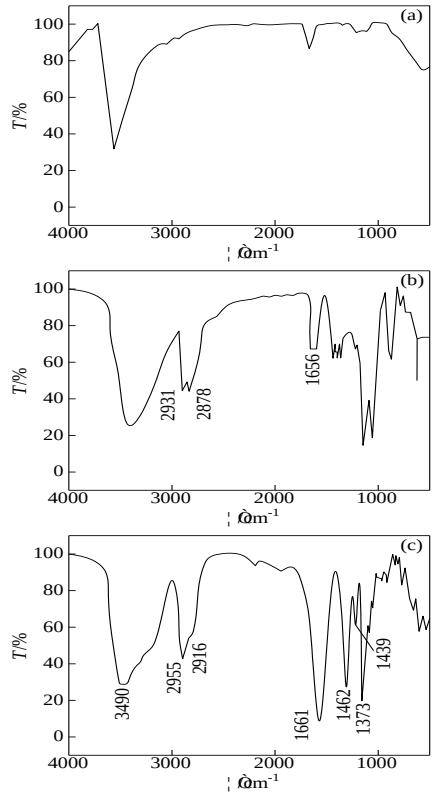

Figure 5: Infrared spectrum analysis of nano copper powder and PVP

As shown in Fig. 3(b), there is a broad absorption peak in the range of 2950-3500/cm, which corresponds to the -OH bond of the aqueous solution. It is suggested that the original nano-copper particles prepared in this paper still remain some organic solvent on the surface. While the diffraction peak in Fig. 3(a) disappears completely; Figure 3(b) shows relatively lower peak shift of -C=O and -C-H groups at 1650/cm and 2925/cm as compared to Figure 3(a). As described above, both cases suggest that the nano copper particles after the secondary treatment have shed off residues on the surface.

As shown in Fig. 6, the thermogravimetric curve of nano copper inks is given. It is obvious that nano copper has a significant mass loss at 145°C, 207°C, 341°C, and 412°C. However, when the temperature exceeds 412°C, the mass of nano copper remains intact, which implies that at 412°C, the organic matters mixed in the nano-copper have completely volatilized. So eventually, the content of decomposition product of nano coppers reaches 46.5% of the original sample.

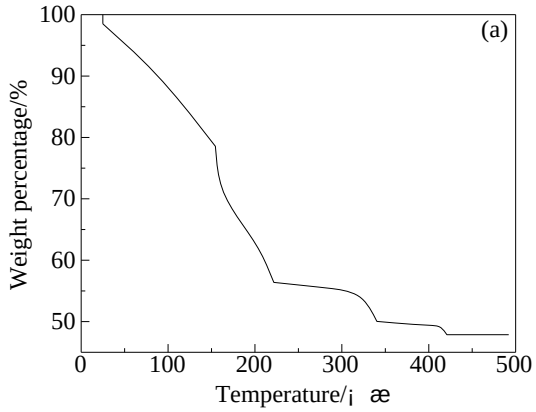

Figure 6: Thermogravimetric curve of nano copper conductive ink

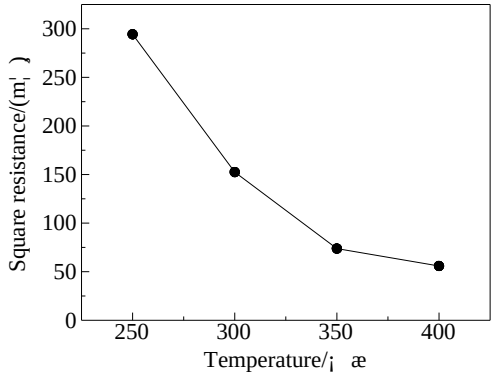

Figure 7: Curve of sheet resistance of nano-copper conductive ink as a function of sintering temperatures (sintered for 15 min)

The prepared nano-copper conductive ink is smeared on the polyimide surface to form a thin film. See Fig. 7 for the sheet resistance curve of the film sintered at different temperatures. Fig. 8 shows the relationship between the sintering time and the sheet resistance when fixed sintering temperatures are 350° C and 400° C, respectively. As shown in the figure, as the sintering temperature rises, the sheet resistance of the film swoops at 250°C ~ 350°C, from 297mΩ to 75.6mΩ; but significantly retards at 350°C ~ 400°C, and down to 56.1 mΩ at 400°C. As the sintering extends, the sheet resistance of the film gets less and less. It is suggested that when the sintering temperature exceeds the melting point of nano-copper, a stable conductivity channel is formed on the surface of the film. After that, the film sintering has no obvious effect on the conductivity any more.

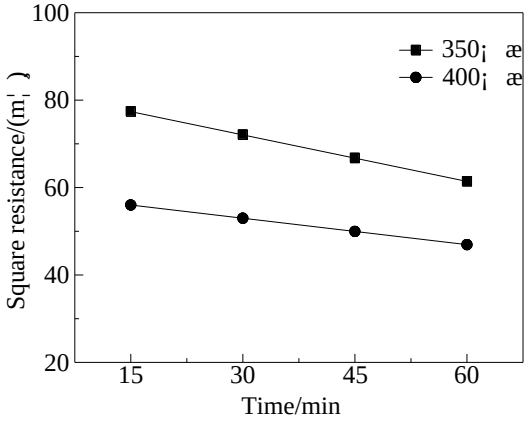

Figure 8: Curve of sheet resistance of nano copper conductive ink as a function of sintering time

4. Conclusions

In this paper, an improved liquid-phase chemical deoxidization is used to prepare nano-copper powde as main conductive material to replace nano-silver particles in the conductive ink. The prepared nano copper particles are analyzed to probe into their microstructure and conductivity. The findings come here as follows:

(1) The prepared nano-copper particles are chain-like with an average particle size of 26 nm. As for particle distribution, those with 20-25nm amount to 42%, 25-30nm to 29%. PVP surfactant can effectively organize the oxidation of nano-copper.

(2) After the sintering temperature exceeds 412°C, the organic matters mixed in the nano-copper have completely volatilized. The content of final decomposition product of nano coppers is 46.5% of the original sample. The higher the sintering temperature, the lower the sheet resistance of the conductive copper film. After the sintering temperature exceeds the melting point of nano-copper, there will be a stable conductivity channel formed on the surface of the film. Afterwards, the film sintering has no obvious effect on its conductivity any more.

Acknowledgments

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